Charge ordering and long-range interactions in layered transition metal oxides

Branko P. Stojković[1], Z. G. Yu[1], A. R. Bishop[1], A. H. Castro Neto[2] and Niels Grønbech-Jensen[1]
[1] *Theoretical Division and Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[2] *Department of Physics, University of California, Riverside, CA 92521*
(February 7, 2008)

We study the competition between long-range and short-range interactions among holes within the spin density wave picture of layered transition metal oxides. We focus on the problem of charge ordering and the charge phase diagram. We show that the main interactions are the long-range Coulomb interaction and a dipolar short-range interaction generated by the short-range antiferromagnetic fluctuations. We find four different phases depending on the strength of the dipolar interaction and the density of holes: Wigner crystal, diagonal stripes, horizontal-vertical stripes (loops) and a glassy-clumped phase. We discuss the effect of temperature, disorder and lattice effects on these phases.

PACS numbers: 71.10.Hf, 71.20.Be, 71.10.-w

Recently there has been much interest in the charge ordering and domain wall formation at mesoscopic scales in doped transition metal oxides [1]. A popular example of such orderings are stripes, i.e., linear arrays of holes separated by an antiferromagnetically (AF) ordered background. The formation of domain walls and stripes has been discussed in terms of the proximity to phase separation [2]. Macroscopic phase separation has been observed in $La_2CuO_{4+\delta}$ [3], and stripes have been observed experimentally in $La_{2-x}Sr_xNiO_{4+y}$ in many different experiments including direct high-resolution electron diffraction [4]. Magnetic susceptibility measurements [5], nuclear quadrupole resonance [6] and muon spin resonance [7] indicate formation of domains in $La_{2-x}Sr_xCuO_4$. Stripes have also been seen in $La_{1-x}Ca_xMnO_3$ for specific commensurate values of doping [8]. A direct evidence for stripe formation was observed in neutron scattering in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ [9]. Moreover, recent neutron scattering experiments are not inconsistent with stripe phases in other high temperature superconductors such as $YBa_2Cu_3O_{7-\delta}$ [10,11].

On the theoretical side, stripes have been proposed as a result of a competition between short-range attractive interaction between holes from the breaking of AF bonds and the long-range Coulomb interaction [12]. Indirect support for this picture has been given in terms of the mapping of the problem into effective spin models [13]. Striped phases have been obtained within mean field approaches to the short-range Hubbard or $t-J$ models which are only able to generate insulating states [14]. Numerical methods in these models have not been able to confirm this picture except for recent Density Matrix Renormalization Group simulations (DMRG) [15].

In this paper we present a numerical approach to the problem of holes moving in an AF insulator in the presence of long-range Coulomb forces. The ability to handle long-range Coulomb interactions at finite density has been enhanced recently in the area of molecular physics: assuming a computational cell of arbitrary geometry and cyclic boundary conditions it is possible to sum interactions of particles with all of their images residing in cells obtained by translation from the original computational cell [16,17]. On making integral transformations, Coulomb interactions are computed by summing over fast-convergent Bessel functions with great accuracy.

Using Monte Carlo (MC) and molecular dynamics (MD) methods, we systematically study the interplay between long-range Coulomb interaction and short-range AF interactions of dipolar nature which we take to have both isotropic and anisotropic components (depending on the lattice structure). Our main result is summarized in the phase diagram of Fig.1. In the absence of disorder we find four phases depending on the density of holes and the characteristic AF energy scales: a Wigner crystal, diagonal stripes, horizontal-vertical stripes (loops) and a glassy-clumped phase. The order parameter for charge ordering is the Fourier transform of the hole density:

$$\rho(\mathbf{q}) = \frac{1}{N}\sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i}\,, \tag{1}$$

where $\mathbf{r}_i$ is the position of the i^{th} hole and N is the total number of holes. A peak in $\rho(\mathbf{q})$ at some wave-vector $\mathbf{q}=\mathbf{K}$ indicates ordering.

Our starting point is the spin density wave (SDW) picture of the layered transition metal oxides which has been very successful in describing the insulating AF phase of these systems [18,19]. In this picture the electrons move with hopping energy t in the self-consistent staggered field of its spin. Because the translational symmetry of the system is broken, the electronic band is split into upper and lower Hubbard bands [20]. These are separated by the Mott-Hubbard gap, Δ, and at half filling the lower band is filled and the upper one is empty. This picture is consistent with the angle resolved photoemission data in the layered AF insulator $Sr_2CuO_2Cl_2$ [21]. By doping the system with holes with planar density σ_s and at low temperatures, T ($k_BT << \Delta$), we

focus entirely on the lower band which has a maximum at $\mathbf{k} = \mathbf{Q}/2 = (\pm 1, \pm 1)\pi/(2a)$, where a is the lattice spacing. It can be shown that the holes interact via two different mechanisms: a short-range attractive force due to AF bond breaking and a long-range dipolar interaction due to the distortion of the AF background [19,22]. It was shown that this dipolar interaction gives rise to spiral distortions of the AF background [22,23]. The dipole moment associated with each hole is due to the virtual hopping of holes between neighboring sites and scales with the AF magnetic energy. The dipolar interaction between two holes with dipole moments $\mathbf{d}_{1,2}$ at distance $\mathbf{r}$ apart has the form:

$$U_{dip} = \frac{1}{r^2}\left[(\mathbf{d}_1 \cdot \mathbf{d}_2) - \frac{2}{r^2}(\mathbf{d}_1 \cdot \mathbf{r})(\mathbf{d}_2 \cdot \mathbf{r})\right], \qquad (2)$$

which is rotationally invariant. It is also possible to show using Ward identities that the spin part of the problem can be described by a two dimensional (2D) non-linear σ model in the long wavelength limit [24]. At finite T the system is magnetically disordered and characterized by a finite magnetic correlation length, ξ [25]. Thus, at finite T the dipolar interaction between the holes, mediated by the antiferromagnet, is actually short-ranged. However, besides the AF interactions the holes also feel the long-range Coulomb interaction. This is clear if we consider that $r_s = r_0/a_0$ (where r_0 is the mean inter-particle distance and a_0 is the Bohr radius) is very large in the underdoped systems ($r_s \approx 8$). Thus, the interaction energy between the holes, which behaves like $e^2/(a_0 r_s)$, is certainly more important than the kinetic term ($\approx e^2/(a_0 r_s^2)$) at low densities. This implies that the interaction terms should be treated first and the kinetic energy as a perturbation. Finally, each hole carries a spin degree of freedom as well, but it is possible to show that the overall spin energy is minimized in the spin anti-symmetric channel, as we assume here. Thus, in our approach, we are left with only the charge channel and the interaction between two holes, 1 and 2, has the form (see Eq. (2))

$$V(\mathbf{r}) = \frac{q^2}{r} - A\, e^{-r/a} - B\cos(2\theta - \phi_1 - \phi_2)e^{-r/\xi}, \qquad (3)$$

where q is the hole charge, θ is the angle made between $\mathbf{r}$ and a fixed axis and $\phi_{1,2}$ are the angles of the dipoles relative to the same fixed axis. A is the strength of the short-range bond-breaking interaction and B is the strength of the dipolar interaction, which we will assume to be independent variables. The magnetic correlation length ξ is obtained from neutron scattering measurements [26]. It is also worth mentioning that the 1/2-filled Landau level problem has been mapped into an interacting 2D dipole gas [27]. More recently it was shown that the same type of description is possible for a 2D electron gas even in the absence of a magnetic field [28].

In general, the many-body problem of holes in an AF background is extremely complicated, involving many-particle interaction terms. However, at low densities it is reasonable to assume that the interaction of any two holes is weakly perturbed by other holes, and the total potential energy can be expressed in terms of two-particle energies. Therefore, in our numerical calculations we study the physics of N holes interacting via $V(\mathbf{r})$ as given in (3). We assume a rectangular computational box of size $L_x \times L_y$ with L_x, L_y up to 100 unit cells in a CuO_2 plane. At the beginning of each simulation we place the holes at random and assign to each hole a dipole moment of constant size, but random direction. We find a minimum of the total potential in this system using three different methods: MC method, Langevin MD and a hybrid MC-MD method [29]. All three methods yield essentially the same results. Since the system exhibits several phases (see Fig. 1) for some values of the input parameters, its ground state is not always well defined and may, in fact, depend on the initial and boundary conditions. Hence, in order to rapidly reach a hole configuration with the lowest global minimum energy we perform simulated annealing from high temperatures.

For $B = 0$ we find the Wigner crystal with small distortions to be the state of lowest energy, as expected [30]. The small distortion of the crystal structure is due to the periodicity, which introduces a small spatial anisotropy into the system due to the rectangular shape of the computational box. Increasing A while retaining $B = 0$ reduces the lattice constant of the Wigner crystal until a critical value is reached where holes group together. For $A = 0$ and finite B the situation is quite different. At small B and larger densities the Wigner crystal is unstable and a new phase with diagonal stripes is formed. This phase is characterized by ferro-dipolar order (see Fig. 2a). The situation here is very similar to that observed in $La_{2-x}Sr_xNiO_{4+y}$ [4]. As shown in Fig. 2c, at larger values of B a line stripe is formed, which, with increasing density tends to close into loops, forming a checkerboard pattern. Importantly, the loop formation is accompanied by dipole orientation along the straight portion of a loop with gradual rotation by $\pi/2$ at each corner [31]. Due to the rotation of dipoles at corners the loops interact, and eventually form the checkerboard pattern [32]. The size of the inter-hole distance within a line is determined by the ratio of B and the Coulomb energy; the loop sizes are determined by the hole density alone. These results appear to be consistent with the DMRG solution of the t-J model [15]. If B is increased further the dipolar interaction becomes dominant over the average Coulomb interaction; the well-defined pattern disappears and one observes star shaped clumps of holes, which can, at sufficiently high density, form another geometric structure (e.g., a Wigner crystal of clumps). We remark that in all phases a non-vanishing value of A leads to a decrease in the effective value of B at which the transitions occur (Fig. 1); the isotropic term A alone *never* produces any non-trivial geometric phase (e.g., stripes), even with

inclusion of lattice effects. We find that the transition between the ferro-dipolar and the stripe phase is first order, while other transitions appear to be of second order [33]. The stripe tension of the hole patterns will be quantified elsewhere [33].

In the cases presented above we have assumed uniform dipolar interaction. It is well known that there are orthorhombic and tetragonal distortions in practically all transition metal oxides. In particular static stripe formation has only been observed in the low temperature tetragonal phase of $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ [9]. In order to study the influence of the anisotropy we assume that the dipole sizes along x and y directions have anisotropy α ($\alpha = 1$ corresponds to the isotropic case). Figure 2c shows our solution for $\alpha = 0.8$: the symmetry is broken and a stripe superlattice is formed, with a charge ordering vector $\mathbf{K} = (\pi/\ell)\mathbf{x}$, where ℓ is the inter-stripe distance. In the SDW model the Fourier transform of the magnetization $S(\mathbf{q}) = \langle S_z(\mathbf{q})\rangle$ is slaved to (1) such that a peak at $\mathbf{K}$ in (1) leads to a peak at $\mathbf{Q} \pm \mathbf{K}$ in $S(\mathbf{q})$ [33]. Thus our results yield a neutron peak at $(\pi/a \pm \pi/\ell, \pi/a)$. Assuming twinning, this would imply neutron peaks at $(\pi/a \pm \pi/\ell, \pi/a \pm \pi/\ell)$ in agreement with experiment [11]. The same is obtained in the checkerboard phase (see Figs. 2c and 2d). If one includes the kinetic energy [33], instead of static stripe formation one would obtain dynamical stripes like those believed to exist in $La_2Sr_xCuO_4$. In this case the Fermi surface of the system should be modified by the superlattice formation [34].

Our results are somewhat sensitive to the applied boundary conditions: first, the exact size of the checkerboards depends on its commensuration with the computational box, which, in turn depends on the density. On increasing of the size of the computational box, the checkerboard pattern shown in Fig. 2c acquires point or line defects [33]. This leads to the reduction in the higher order peaks observed in Fig. 2d with no change in their wave-numbers. Second, in a finite system with appropriate charge background, the holes do not form geometric phases, although they still form stripes [33]. However, in this case even a very small anisotropy ($\alpha \sim 0.95$) again leads to stripe formation as in Fig. 2e [33].

We have also studied impurity effects (from defects or charged counter-ions). For example, we place the same number of impurities as holes, randomly in a plane a distance $d = 6\mathring{A}$ above the plane to simulate the situation in, e.g., Sr doped cuprates and consider the *unscreened* attractive Coulomb interaction between impurity and hole. The charge pattern produced is very sensitive to impurity doping (see Fig. 2f). The Wigner crystal becomes glassy with no obvious sign of charge ordering. This happens because the attractive Coulomb energy between impurities and holes scales like e^2/d while the average inter-hole Coulomb energy behaves like $e^2\sqrt{\sigma_s}$. Thus when $\sigma_s < 1/d^2$ the holes are pinned by impurities. Most strikingly, all other phases are unstable towards *finite* stripe formation. The loops and diagonal stripes tend to deform to pass very close to the impurities in order to maximize the attractive energy. However, the dipole interaction is sufficient to retain the main orientation. This leads us to conjecture that with the addition of the kinetic energy the holes can move in string segments in an orientation given basically by the phase diagram of the clean system. These string segments are kept together by the dipolar interaction (i.e., string tension). The stripe motion would then be caused by mesoscopic thermal or quantum tunneling of the finite strings between the minima of the overall potential. This would lead to non-linear effects in the low temperature field dependent conductivity [35] and unusual T dependence of the conductivity [33]. We have also performed simulations in the presence of a realistic underlying periodic lattice and have found that this creates slight distortions in the phases, pinning loops more strongly [33]. In particular, the peaks in $\rho(\mathbf{q})$ sharpen in some of these phases. Finally, at finite T melting of the phases occurs because of the small energy scales and large entropy in long-range Coulomb tails.

In summary, using a novel numerical technique, we have studied the competition between long-range and short-range interactions and its impact on hole ordering in layered transition metal oxides. Employing the SDW picture of these systems, we have studied the short-range attractive force and the dipolar force generated by the short-range AF fluctuations together with long-range Coulomb forces for a 2D layer. We have found a rich phase diagram for the clean system which includes a Wigner solid, stripes, loops and a glassy phase. This phase diagram is consistent with several different experimental measurements. We have also found this system to be rather sensitive to the presence of charged impurities. However, the stripe phases survive as finite stripe segments which we believe is key to understanding these systems. Finally we have also investigated the effects of a periodic lattice, which leads to minor distortions of the various phases. These results are of great importance for the understanding of the phase diagram of layered transition metal oxides.

We gratefully acknowledge valuable discussions with A. Balatsky, A. Chernishev, J. Gubernatis, C. Hammel, D. Pines, J. Schmalian, S. White and J. Zaanen. A. H. C. N. acknowledges support from the Alfred P. Sloan foundation. Work at Los Alamos was supported by the U. S. Department of Energy. Work at the University of California, Riverside, was partially supported by a Los Alamos CULAR project.

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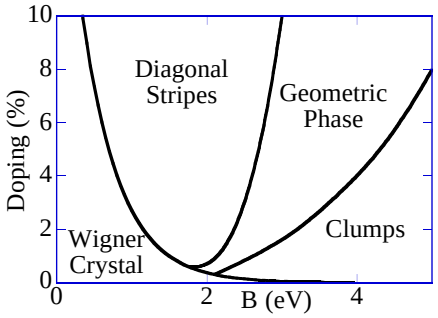

FIG. 1. Phase diagram as a function of the hole density and the strength of the dipolar interaction, B, for $A = 0$.

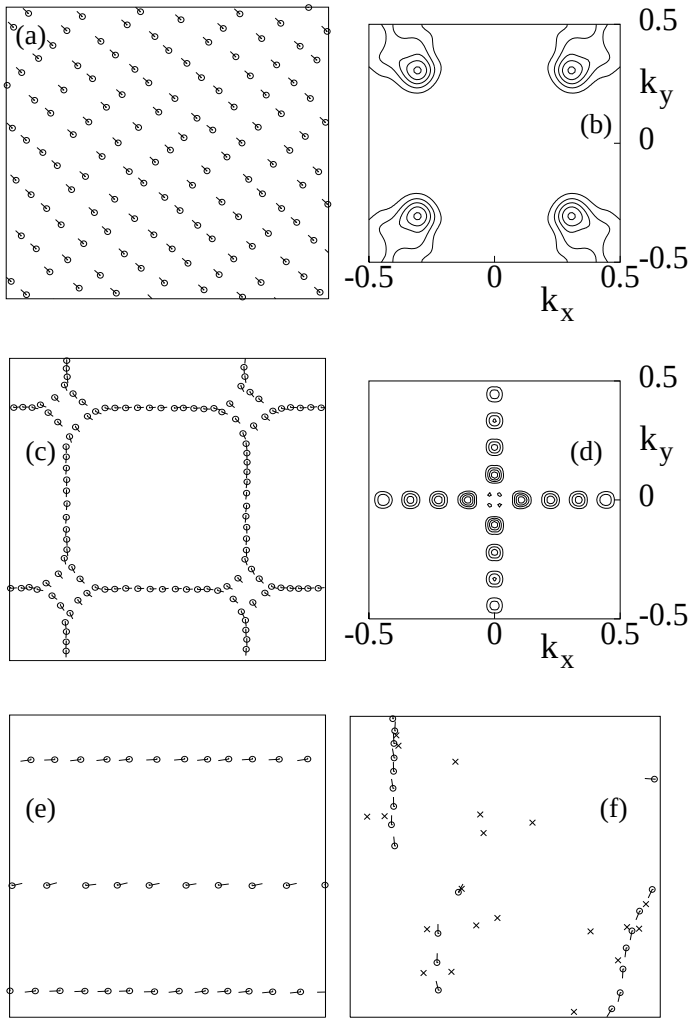

FIG. 2. Geometric phases resulting from the competition of dipolar and Coulomb interactions: panels (a) and (c) show holes (open circles) with their dipole orientations, in a small section of the computational box, for the ferro-dipolar and stripe phases, respectively; panels (b) and (d) show contour plots of the hole density in momentum space (see Eq. (1)) for the phases shown in panels (a) and (c). Panel (e) shows the stripe phase obtained with dipole anisotropy of 0.8, and panel (f) hole positions in the presence of impurities (crosses).